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VISCOMETER

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(57) Claim

1. A method for measuring the viscosity of a fluid, wherein there is an electroactive species in said fluid and wherein said method comprises placing at least one working electrode in the fluid, measuring the limiting steady-state diffusion current produced when an electrode potential is applied to the at least one working electrode, and calculating the viscosity of the fluid from the measured limiting steady state diffusion current.

7. An apparatus for measuring the viscosity of a fluid, which apparatus comprises at least one working electrode to be placed in the fluid, means to apply an electrode potential to the at least one electrode to thereby establish a limiting steady-state diffusion current and means to measure the limiting steady-state diffusion current.

VISCOMETER

The present invention relates to a method and apparatus for measuring the viscosity of a fluid.

Viscosity is a measure of the resistance of fluids to flow. The viscosity of liquids is conventionally measured by one of the following methods:

1) Stokes' Law methods which involve measurement of the rate of fall of a small sphere in a liquid. The viscosity of the liquid is then determined from Stokes law.

2) Capillary tube methods, which involve measuring the flow of a liquid through a capillary. Viscosity is determined by using the Poiseulle equation. Allowance must be made for end effects and the fluid flow through the capillary must be laminar.

3) Rotating cylinder methods, in which the liquid is placed in the annular space between an inner and an outer cylinder. Viscosity of the liquid is determined by measuring the torque transmitted to the stationary inner cylinder when the outer cylinder is rotated at a constant speed.

4) Oscillating disk methods which involve measuring the damping rate of a disk oscillating in a plane parallel to and close to a plane surface.

The present inventors have now developed a novel electrochemical method for measuring the viscosity of a

fluid. The method involves measuring the limiting steady-state diffusion current of an electroactive species dissolved in the fluid, by means of an electrode placed in the fluid, and subsequently calculating the viscosity of the fluid from the measured limiting steady-state diffusion current.

According to one aspect, the present invention provides a method for measuring the viscosity of a fluid, which method comprises placing at least one working electrode in the fluid, measuring the limiting steady-state diffusion current produced when an electrode potential is applied to the at least one working electrode, and calculating the viscosity of the fluid from the measured limiting steady state diffusion current.

In another aspect, the present invention provides an apparatus for measuring the viscosity of a fluid, which apparatus comprises at least one working electrode to be placed in the fluid, means to apply an electrode potential to the at least one electrode to thereby establish a limiting steady state diffusion current and means to measure the limiting steady state diffusion current.

Any electrode that establishes a limiting steady-state diffusion current when an electrode potential is applied to the electrode may be used in the present invention. Examples of suitable electrodes include microelectrodes, thin layer cells, rotating disk electrodes and dropping mercury electrodes. Microelectrodes and thin layer cells are preferred because they have no moving parts. Microelectrodes are especially preferred.

For convenience, the invention will hereinafter be described with reference to microelectrodes. However, it will be appreciated that the invention is not restricted to the use of microelectrodes.

The present invention is based upon the realisation that the limiting steady-state diffusion current (i_L) at a disk microelectrode is directly proportional to the diffusion co-efficient, according to equation (1).

$$i_L = 4n\ F\ D\ r_0\ C \qquad (1)$$

where

n = number of electrons transferred per molecule
F = Faraday's constant
D = diffusion co-efficient of electroactive species in the fluid
r_0 = radius of the disk microelectrode, and
C = bulk concentration of electroactive species in the fluid

The diffusion of the electroactive species in solution is influenced by the solution viscosity (η). The Stokes-Einstein relationship states that the diffusion coefficient of a solution species is inversely proportional to the solution viscosity according to equation (2):

$$D = RT\ /\ (6\ \Pi\ \eta\ r\ N_A) \qquad (2)$$

where:

R = universal gas constant
T = absolute temperature (K)
r = hydrodynamic radius of solution species
N_A = Avogadro's number.

Combining equations (1) and (2) reveals that the steady-state diffusion current is inversely proportional to the solution viscosity (3):

$$iL = \frac{2\ n\ FRT\ r_0\ C}{3\Pi\ N_A\ r\ \eta} \qquad (3)$$

Accordingly, for a given system, the viscosity of a fluid can be calculated from a measurement of the limiting steady-state diffusion current.

From the above discussion, it will be appreciated that the method and apparatus of the present invention for measuring viscosity of a fluid require that an electroactive species be present in the fluid to enable the microelectrode to respond and establish a limiting steady-state diffusion current. The electroactive species may already be present in the fluid as a component of the fluid (e.g. in the case where the fluid contains oxygen) or it may be added to the fluid prior to the viscosity measurement. For example, a mixture of ferricyanide and ferrocyanide ions may be added to the fluid prior to measuring the viscosity. If an electroactive species is added to the fluid, only a small concentration of the electroactive species need be added (e.g. micromolar concentration).

As stated before, microelectrodes are the preferred electrodes for use in the present invention. The microelectrodes may be made from one or more carbon fibres, each having a diameter below 100μm, or may be made according to the designs found in the open literature (e.g. "Microelectrodes: Theory and Applications", Ed. by M.I. Montenegro et al., Kluwer Academic Publishers (Dordrecht) 1991, or "Ultramicroelectrodes", Ed. by M. Fleischmann, Datatech Systems, Inc. (Morganton) 1987).

An array of microelectrodes may also be used. The number of microelectrodes in the array may range from less than 10 to many hundreds of thousands.

The means for calculating the viscosity of the fluid may be a simple calibration curve of limiting steady state diffusion current plotted against viscosity for the fluid in question. More preferably, the calculating means comprises a computer or other electronic device which can compute the viscosity directly from the measured value of limiting steady state diffusion current.

The method and apparatus according to the present invention are suitable only for measuring the viscosity of liquids that are single phases. Such liquids include pure solutions, mixtures of pure solutions, and pure solvents. The method and apparatus for the present invention are not suitable for measuring the viscosities of two-phase systems such as gels and slurries, because the present invention measures the viscosity of the liquid phase only. For example, attempting to measure the viscosity of a gel formed between water and gelatin using the present invention gives the value for the viscosity of water, rather than the value for the viscosity of the gel.

The invention will now be further described with reference to the following non-limiting examples and the Figures in which:

Figure 1 shows a diagram of apparatus in accordance with the invention; it comprises a waveform generator 1 and potentiostat 2 providing an electrode potential to microelectrode array 3 measured with respect to a combined reference/counter electrode 4, both electrodes being placed in solution 5 held in beaker 6. The limiting steady-state diffusion current is displayed on pen recorder 7.

Figure 2 shows cyclic voltammograms of a mixture of 0.01 molar potassium ferrocyanide and 0.01 molar potassium ferricyanide in purely aqueous media; scan rate=10 mV/s. (a) seven-fibre array; (b) large array.

Figure 3 shows cyclic voltammograms of a mixture of 0.01 molar potassium ferrocyanide and 0.01 molar potassium ferricyanide in different solutions; seven fibre array. (a) 76% glycerol, 10 mV/s; (b) 96% glycerol, 10 mV/s; and (c) 96% diglycerol, 10 mV/s.

Figure 4 shows cyclic voltammograms of a mixture of 0.01 molar potassium ferrocyanide and 0.01 molar potassium ferricyanide in different solutions; large array. (a) 76% glycerol, 10 mV/s; (b) 75.5% d-sorbitol, 10 mV/s; and (c) 96% diglycerol, 2 mV/s.

Figure 5 shows reciprocal limiting steady-state diffusion currents (normalised with respect to their values in purely aqueous solutions) versus bulk solution viscosities. The point at the origin corresponds to pure water.

Examples

A number of solutions were prepared using glycerol, potassium chloride, diglycerol and d-sorbitol. Analytical reagent grade potassium ferricyanide and potassium ferrocyanide trihydrate were added to each solution to provide the electroactive species. Doubly distilled, organic free water was used to prepare the solutions. All solutions contained 0.10 molar potassium chloride to decrease solution ohmic drop.

The bulk viscosities of the solutions were measured using a Brookfield LVT synchro-lectric viscometer, mounted on a Brookfield helipath stand and using a PTFE-coated spindle #1 (Brookfield Engineering Laboratories, Stoughton, MA, USA). A water jacketed cell was used to maintain the solutions at 250C for both the viscosity measurement (using the Brookfield viscometer) and the electrochemical measurement (using the apparatus of Figure 1). Three hundred millilitres of solution were used in all measurements.

The electrochemical equipment of Figure 1 consisted of a Model 173 potentiostat/galvanostat, a Model 175 universal programmer (both Princeton Applied Research, USA) and an HP 7054 A X-Y recorder (Hewlett Packard). A home-built current amplifier (amplification 1000x) was inserted between the microelectrode array and the potentiostat as required.

Two microelectrode arrays were prepared: a small array consisting of 7 carbon fibres and a large array consisting of an uncounted number of fibres (but numbering in the tens of thousands).

A platinum wire electrode served as a combined reference-counter electrode.

Typical cyclic voltammograms in unstirred purely aqueous solutions of 0.01 molar potassium ferricyanide - 0.01 molar potassium ferricyanide mixture at the small and large microelectrode arrays are shown in Figure 2. The steady-state behavior is clearly evident at the small array (curve a). The voltammogram at the large array (curve b) exhibited pronounced hysteresis between the cathodic and anodic scans at the scan rate used. A steady-state limiting current measurement at the large array was obtained by holding the potential at the limiting current region for five minutes.

Figures 3 and 4 show cyclic voltammograms of 0.01 molar ferricyanide-ferrocyanide mixture in solutions of different viscosities.

To remove the influence of differences in electrode surface area between electrodes, steady-state limiting diffusion currents were normalised with respect to the steady-state limiting diffusion currents observed for the same electrodes in aqueous solutions. The resulting relationship between the reciprocal normalised steady-state limiting diffusion current and solution viscosity is shown in a log-log plot in Figure

5. Excellent straight-line relationships were observed in each case.

The diffusion of iron cyanide complexes in solutions of different viscosities conformed well to equation 3. Moreover the huge number of microelectrodes in the large array facilitated the measurement of the very low current levels in the most viscous solutions. Overall the results demonstrate that microelectrode arrays can serve as viscosity-measuring devices in solutions containing electroactive species.

Those skilled in the art will appreciate that the invention is susceptible to variations and modifications other than those specifically described. It is therefore to be understood that the invention includes all such variations and modifications that fall within its spirit and scope.

The claims defining the invention are as follows:-

1. A method for measuring the viscosity of a fluid, wherein there is an electroactive species in said fluid and wherein said method comprises placing at least one working electrode in the fluid, measuring the limiting steady-state diffusion current produced when an electrode potential is applied to the at least one working electrode, and calculating the viscosity of the fluid from the measured limiting steady state diffusion current.

2. A method according to claim 1 wherein the at least one electrode is selected from microelectrodes, thin layer cells, rotating dish electrodes and dropping mercury electrodes.

3. A method according to claim 1 wherein the at least one electrode is a microelectrode.

4. A method according to any one of the preceding claims wherein an array of electrodes are used.

5. A method according to any one of the preceding claims wherein an electroactive species is added to the fluid prior to measuring the limiting steady-state diffusion current.

6. A method according to claim 5 wherein the electroactive species added to the fluid comprises a mixture of ferricyanide and ferrocyanide ions.

7. An apparatus for measuring the viscosity of a fluid, which apparatus comprises at least one working electrode to be placed in the fluid, means to apply an electrode potential to the at least one electrode to thereby establish a limiting steady-state diffusion

current and means to measure the limiting steady-state diffusion current.

8. An apparatus according to claim 7 wherein the at least one electrode is selected from microelectrodes, thin layer cells, rotating disk electrodes and dropping mercury electrodes.

9. An apparatus according to claim 7 wherein the at least one electrode is a microelectrode.

10. An apparatus according to any one of claims 7 to 9 wherein said apparatus comprises an array of electrodes.

11. An apparatus according to any one of claims 7 to 10 wherein the means to apply an electrode potential comprises a potentiostat.

12. An apparatus according to any one of claims 7 to 11 wherein the means to measure the limiting steady-state diffusion current comprises a reference electrode.

13. An apparatus according to any one of claims 7 to 12 further including means to calculate the viscosity of the fluid.

14. A method according to claim 1 substantially as hereinbefore described with reference to any one of the figures or examples.

15. An apparatus according to claim 7 substantially as hereinbefore described with reference to any one of the figures.

Dated this 6th day of January 1993.

COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION.

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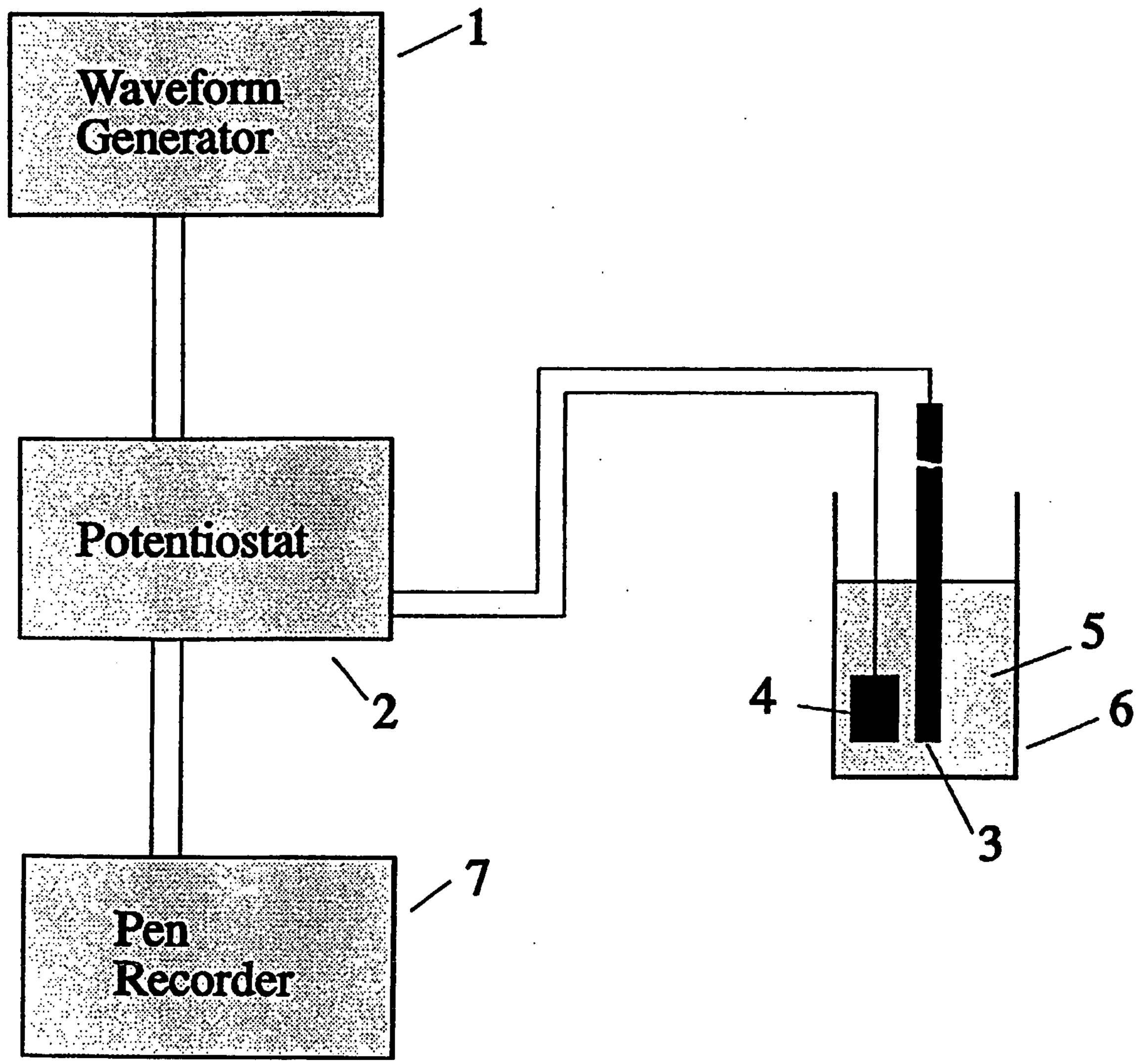
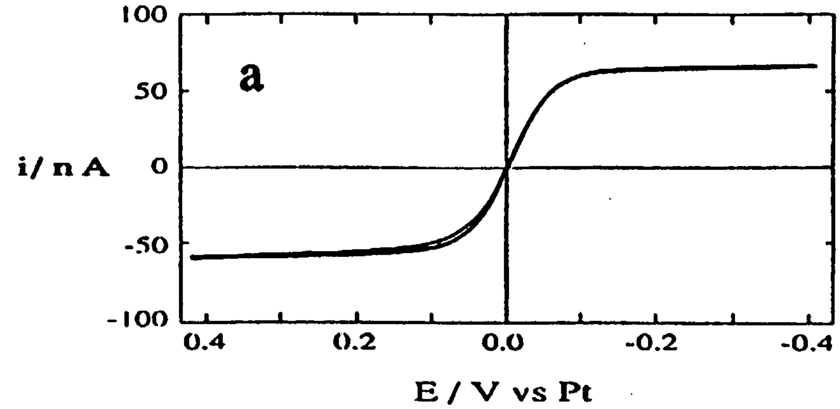


Figure 1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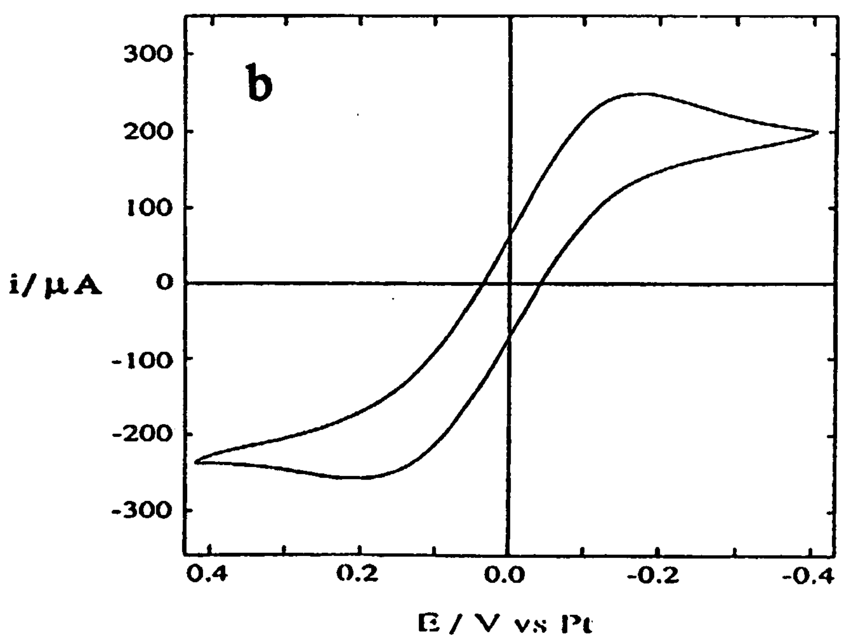
E / V vs Pt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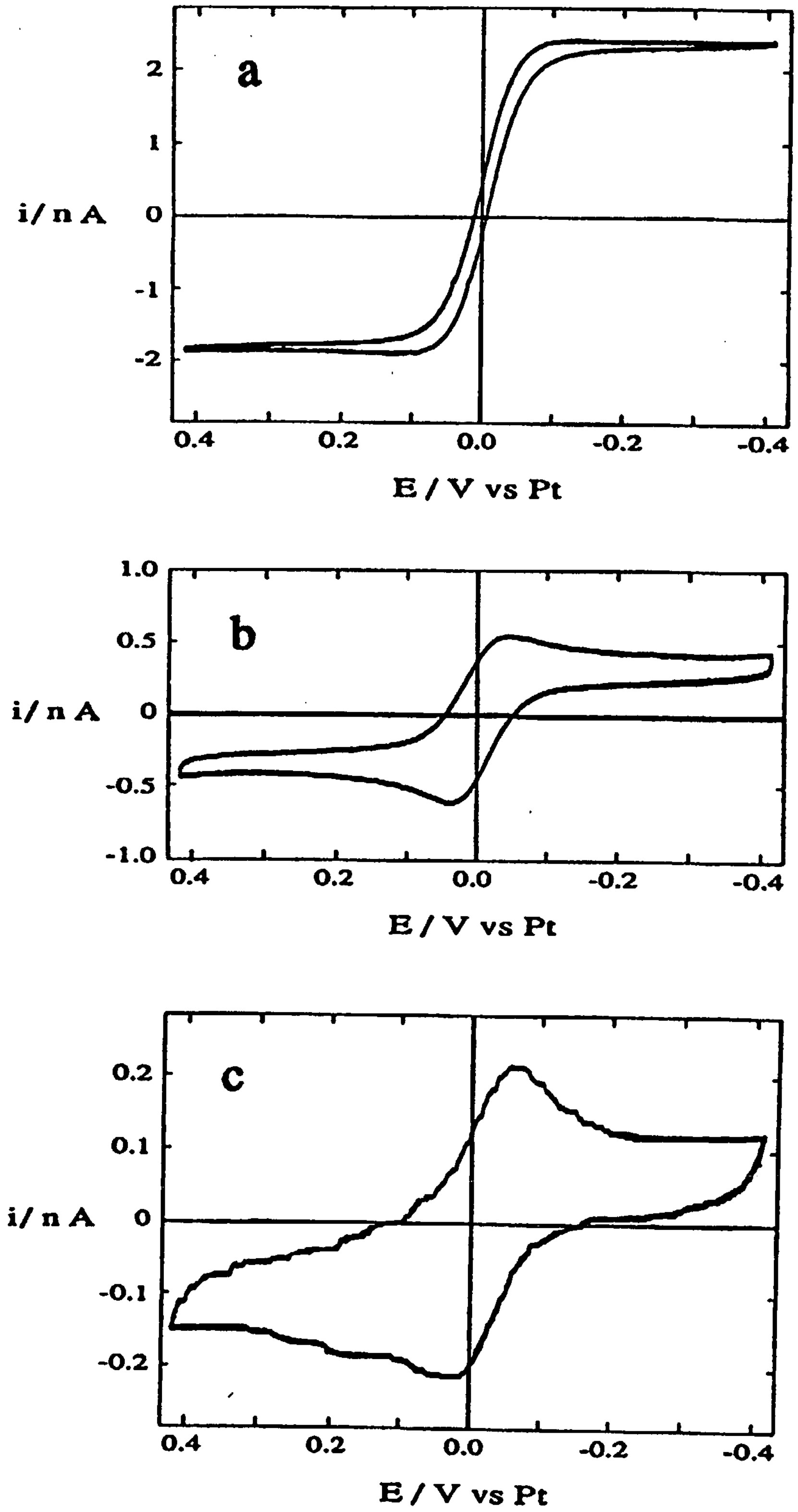
E / V vs Pt

Figure 2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0.0
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-0.4
E / V vs Pt
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i/ n A
1.0
0.5
0
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-1.0
0.4
0.2
0.0
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E / V vs Pt
c
i/ n A
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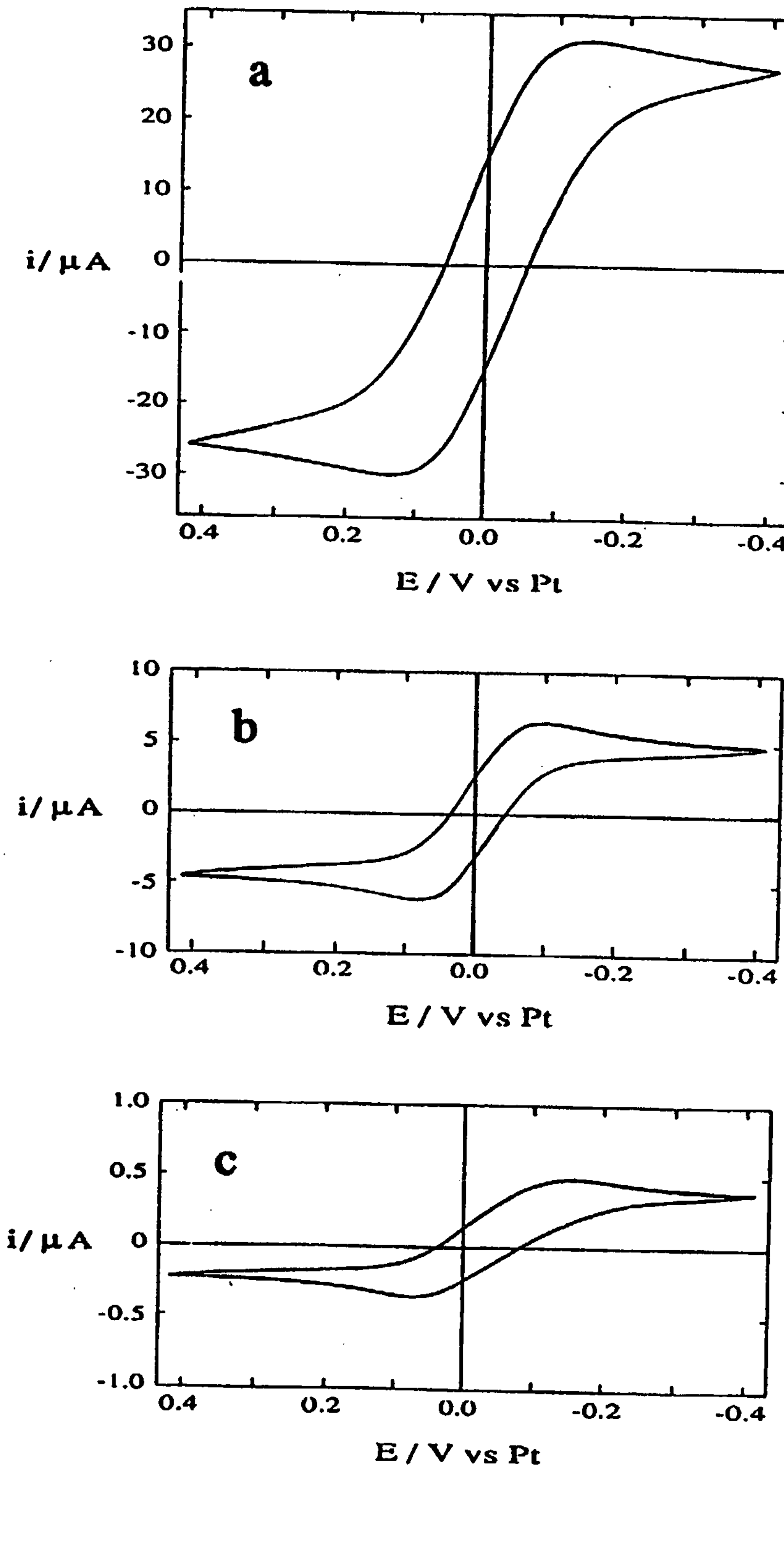
-0.2
0.4
0.2
0.0
-0.2
-0.4
E / V vs Pt

Figure 3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i/μA
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5
0
-5
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0.4
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E / V vs Pt

Figure 4